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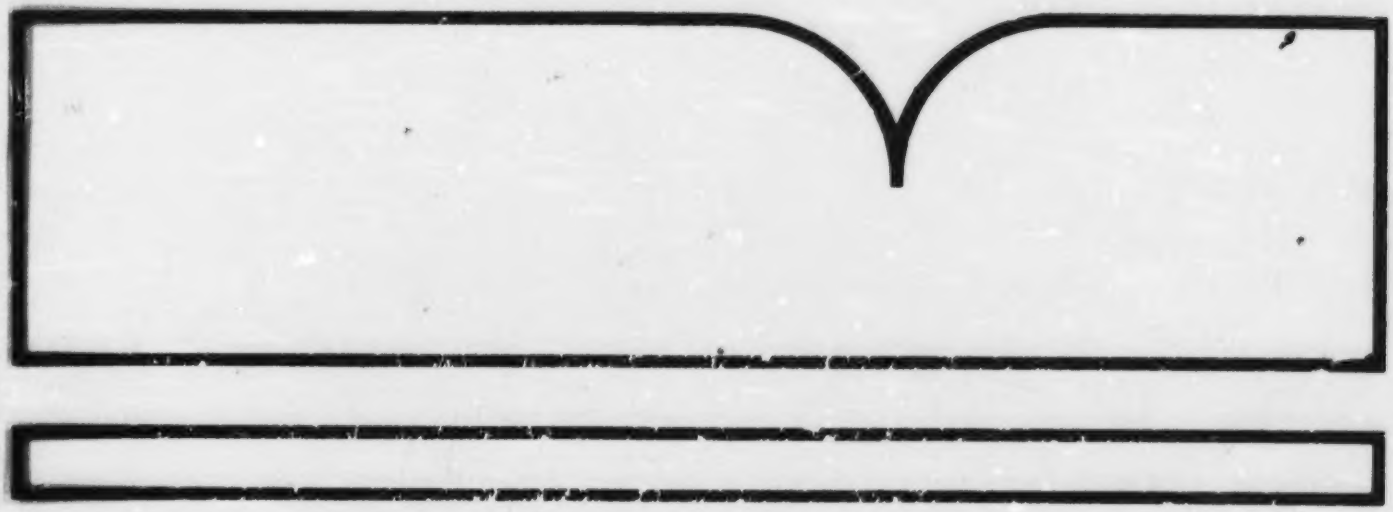

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FATE OF CHEMICALS IN AQUATIC SYSTEMS: PROCESS MODELS AND COMPUTER CODES

by

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16. ABSTRACT

Aquatic fate models are designed to forecast the residual concentrations, dominant pathways, distributions among subsystems, and characteristic time scales of xenobiotic chemicals. Most are constructed as systems of differential equations organized around mass balances. The resulting computer codes are used as aids in chemical use and disposal evaluations; their primary function is to reduce complex chemical and environmental data sets to useful forms. Relevant chemical phenomena include direct and indirect photochemical reactions, hydrolytic processes, biotransformations, ionic speciation, and sorption. These phenomena include both reversible and irreversible processes, with a mixture of time scales ranging from the virtually instantaneous to the imperceptible, depending on the structure and reactivity of the chemical involved. Aquatic transport processes include hydrodynamic transport of dissolved materials, entrained transport of chemicals sorbed with particulates, volatilization, and exchange across the benthic boundary layer. The models combine chemical partitioning and rate constants with environmental driving forces, yielding a set of differential equations that can be analyzed to reveal chemical behavior as a function of time, space, and extrinsic chemical loadings.

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Fate of Chemicals in Aquatic Systems: Process Models and Computer Codes

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Aquatic fate models are designed to forecast the residual concentrations, dominant transformation pathways, distributions among subsystems, and characteristic time scales of xenobiotic chemicals. Most are constructed as systems of differential equations organized around mass balances. The resulting computer codes are used as aids in chemical use and disposal evaluations; their primary function is to reduce complex chemical and environmental data sets to useful forms. Relevant chemical phenomena include direct and indirect photochemical reactions, hydrolytic processes, biotransformations, ionic speciation, and sorption. These phenomena include both reversible and irreversible processes, with a mixture of time scales ranging from the virtually instantaneous to the imperceptible, depending on the structure and reactivity of the chemical involved. Aquatic transport processes include hydrodynamic transport of dissolved materials, entrained transport of chemicals sorbed with particulates, volatilization, and exchange across the benthic boundary layer. The models combine chemical partitioning and rate constants with environmental driving forces, yielding a set of differential equations that can be analyzed to reveal chemical behavior as a function of time, space, and extrinsic chemical loadings.

When emitted to the aquatic environment, pesticides may endanger native populations and downstream drinking water supplies. A realistic evaluation of such dangers requires a knowledge of the transport and transformation processes that govern the exposure of organisms to chemical residuals. Exposure, fate, and persistence can be estimated via appropriately designed computer programs,

thus providing an objective, rational, and replicable framework for chemical use and disposal decisions (1).

Aquatic fate models must account for several kinds of phenomena, including transport and transfer processes that move a compound among ecosystem segments and compartments, and degradation processes that convert the compound to transformation products. This chapter provides a brief summary of the quantitative basis for describing these processes, a description of the logic and data structures used to assemble fate codes, and a brief catalog of some of the main publicly available, better documented computer programs for aquatic fate.

Transport and Transfer Processes

Ionization, sorption, volatilization, and entrainment with fluid and particle motions are important to the fate of synthetic chemicals. Transport and transfer processes encompass a wide variety of time scales. Ionizations are rapid and, thus, usually are treated as equilibria in fate models. In many cases, sorption also can be treated as an equilibrium, although somtimes a kinetic approach is warranted (2). Transport processes must be treated as time-dependent phenomena, except in simple screening models (3,4).

Hydrodynamic Transport. Hydrodynamic transport is often modeled as a combination of advection and dispersion. Advection, the flow of water through the system, is usually represented via the mean flow velocity of a river, or hydraulic discharge from a lake or pond. Dispersion, an analogy with molecular diffusion, is a statistical accounting of the effects of turbulence, storm surges, internal waves, and other phenomena not amenable to detailed, mechanistic descriptions. The study of hydrodynamics is best developed for rivers (5) and estuaries (6), although the hydromechanics of ponds and lakes has not been totally neglected (7). Hydrodynamic flows carry an entrained load of dissolved materials. The transport of dissolved synthetic chemicals can be readily derived by regarding the flow as a simple carrier. In many instances a model for synthetic chemicals can be "piggy-backed" on either a hydrodynamic transport model or on a transport description derived from observational data.

Ionization. Many organic chemicals contain functional groups that dissociate to yield charged species. The toxicity and chemical reactivity of the uncharged (neutral) molecule and its charged ions can be very different. Differences in reactivity of ionic species can be accommodated in fate models when rate constants are expressed in terms of the individual species.

Ionization equilibria of acids and bases can be computed fairly easily. Consider, for example, an acid HA (H the hydrogen atom and A the remainder of the molecule). The distribution of HA between its un-ionized [HA] and ionized [A^-] species is controlled

by the pH of the solution. Letting "I" denote the "ionization fractions" (8):

$$Io = 1 / (1 + Ka/[H^+]) = [H^+]/([H^+] + Ka) \quad (1)$$

where Io is the fraction present as HA and Ka is the "ionization" or "acidity" constant. Mass conservation requires that the remainder be equal to (1 - Io); this fraction can also be expressed as $Ka/([H^+]+Ka)$. This concept of "ionization fractions" (or more generally, equilibrium species distribution fractions) can be extended to include the simultaneous occurrence of multivalent anions and cations, sediment-sorbed and biosorbed equilibrium states, etc.

Sorption. Capture of neutral organics by non-living particulates depends on the organic carbon content of the solids (9). Equilibrium sorption of such "hydrophobic" compounds can be described by a carbon-normalized partition coefficient on both a whole-sediment basis and by particle size classes. The success of the whole-sediment approach derives from the fact that most natural sediment organic matter falls in the "silt" or "fine" particle size fractions. So long as dissolved concentrations do not exceed 0.01 mM, linear isotherms (partition coefficients) can be used. At higher concentrations, the sorptive capacity of the solid can be exceeded, and a nonlinear Freundlich or Langmuir isotherm must be invoked.

Sorption of ionizable compounds (organic acids and bases) has yet to be described as a function of independent properties of compounds and environments. Ionization itself is quite fast and can be described as a simple equilibrium. The sorption of the resulting ions involves competition with normal inorganic and organic cations and anions. Sorption of organic cations can be described fairly well via a competitive Langmuir isotherm, using cation exchange capacity (CEC) as a general capacity factor (10). Given partition coefficients for neutral and ionic species, computation of the (local) equilibrium distribution of a compound is straightforward. Nonlinear isotherms and detailed sorption kinetics (2) have yet to be incorporated in operational exposure models, however, although some programs include a first-order kinetic approximation.

Particle Transport. Because many organic chemicals bind with aquatic particulate matter, particle transport can determine the fate of compounds. Sediment transport has been of interest to the engineering profession for many years. Many discussions of the dynamics of fluvial sediment transport have appeared in the literature (11, 12). As with hydrodynamic transport, one strategy for environmental modeling is to "piggy-back" the transport of sorbed chemicals on a model of transport of the sediment phase.

Interactions with Benthic Subsystems. In many lakes and coastal seas, net sediment deposition can be very slow. In these cases, capture of synthetic compounds may be driven primarily by the activities of the biota, including physical disturbance by demersal fishes, irrigation of the sediments by benthic macrofauna (13), and sorption to surface layers followed by subduction and mixing of contaminated layers by crustacea and worms. In addition, physical stirring via sediment "bursting" (14, 15) can facilitate exchange across the benthic interface. In general, transport across the benthic boundary layer can be described via an advection/dispersion equation (16), in which the advection term accounts for ground-water flow and exchange events are described via a dispersion term.

Biosorption and Bioaccumulation. Food chain transmission of pollutants, and direct pollutant transfer to otherwise uncontaminated populations (e.g., human consumption of contaminated fishes), result from biosorption and bioaccumulation of xenobiotic chemicals. In the case of microorganisms, with their very high surface to volume ratio, capture of synthetic organics can be described via a partition coefficient (17). Simple partitioning probably can be used to describe uptake of synthetic organics by the majority of organisms occupying the base of aquatic food chains. The uptake of pollutant chemicals by higher organisms is complicated by the presence of multiple dietary and direct routes of exposure, including transport across gill membranes and, at least for marine fishes, direct water intake. The significance of partitioning, as against dietary uptake, must vary with the physiology and life history of the organism. For example, blue crabs (Callinectes) take up little or no Kepone via direct absorption from seawater, but readily accumulate this compound via dietary intake (18). Although simple bioconcentration factors are adequate for many purposes, detailed exposure models probably should include some capability for representing dietary exposures (19), biosorption or membrane transfers, and depuration, metabolism, and detoxification.

Volatilization. Transfer of chemicals across the air/water interface can result in either a net gain or loss of chemical, although in many cases the bulk concentration in the air above a contaminated water body is low enough to be neglected (20). When the atmosphere is the primary source of the contaminant, as for example polychlorinated biphenyls in some parts of the Laurentian Great Lakes, atmospheric concentrations obviously cannot be neglected. The Whitman two-film or two-resistance approach (21) has been applied to a number of environmental situations (20, 22, 23). Transport across the air/water interface is viewed as a two-stage process, in which both phases of the interface can offer resistance to transport of the chemical. The rate of transfer depends on turbulence in the water body and in the atmosphere, the

Henry's Law constant of the chemical, and the molecular velocity of the compound in the near-surface regions.

Transformation Processes

Direct Photolysis. Direct photochemical reactions are due to absorption of electromagnetic energy by a pollutant. In this "primary" photochemical process, absorption of a photon promotes a molecule from its ground state to an electronically excited state. The excited molecule then either reacts to yield a photoproduct or decays (via fluorescence, phosphorescence, etc.) to its ground state. The efficiency of each of these energy conversion processes is called its "quantum yield"; the law of conservation of energy requires that the primary quantum efficiencies sum to 1.0. Photochemical reactivity is thus composed of two factors: the absorption spectrum, and the quantum efficiency for photochemical transformations.

The rate of photolytic transformations in aquatic systems also depends on the intensity and spectral distribution of light in the medium (24). Light intensity decreases exponentially with depth. This fact, known as the Beer-Lambert law, can be stated mathematically as: $d(Eo)/dZ = -K(Eo)$, where Eo = photon scalar irradiance (photons/cm^2/sec), Z = depth (m), and K = diffuse attenuation coefficient for irradiance (/m). The product of light intensity, chemical absorptivity, and reaction quantum yield, when integrated across the solar spectrum, yields a pseudo-first-order photochemical transformation rate constant.

Indirect Photolysis and Oxidation. The simultaneous occurrence of "humic materials," dissolved oxygen, and sunlight often results in an acceleration of the rate of transformation of organic pollutants (25, 26). These reactions are termed "indirect" or "sensitized" photolysis. Indirect photolysis can be subdivided into two classes of reactions. First, "sensitized photolysis" per se involves excitation of a (humic) sensitizer by sunlight, followed by direct chemical interaction between the sensitizer and a pollutant. The second class of indirect photolysis involves the formation of chemical oxidants, primarily via the interaction of sunlight, humic materials, and dissolved oxygen (27). The primary oxidants known to occur in natural waters are hydroxyl and peroxy radicals (28) and singlet oxygen (29). Aquatic fate codes represent the oxidative transformation of pollutants via a purely phenomenological coupling of a second-order rate constant (with units /M/time) to the concentration (moles/liter) of oxidants in the system. The occurrence and concentration of oxidants in natural waters has been investigated via the laboratory irradiation of chemical "probes" (28, 29, 30).

Hydrolysis. Hydrolysis of synthetic organics occurs via several pathways. Specific-acid and -base catalyzed processes can be

described in terms of pH and temperature (31). Neutral hydrolysis (i.e., pH-independent mechanisms) can proceed either via direct reactions involving the water molecule in the rate-limiting step or via indirect molecular transformations involving water as a reactant. (Both are apparent first-order reactions.) The information required by fate models can be encapsulated in a pH-rate profile (Figure 1). Hydrolysis kinetics are readily described via second-order equations incorporating the effects of temperature and ionization on chemical reactivity.

General acid/base catalysis is less significant in natural fresh waters, although probably of some importance in special situations. This phenomenon can be described fairly well via the Brönsted law (relating rate constants to pKa and/or pKb of general acids and bases). Maximum rates of general acid/base catalysis can be deduced from a compound's specific acid/base hydrolysis behavior, and actual rates can be determined from relatively simple laboratory experiments (34).

Microbial Biotransformation. Microbial population growth and substrate utilization can be described via Monod's (35) analogy with Michaelis-Menten enzyme kinetics (36). The growth of a microbial population in an unlimiting environment is described by: $dN/dt = u\,N$, where u is called the "specific growth rate" and N is microbial biomass or population size. The Monod equation modifies this by recognizing that consumption of resources in a finite environment must at some point curtail the rate of increase (dN/dt) of the population:

$$u = u(max) \frac{[S]}{Ks + [S]} \qquad (2)$$

in which [S] is the concentration of the growth-limiting substrate, u(max) is the "maximum specific growth rate" attained when [S] is present in excess (i.e., non-limiting), and Ks, the "saturation constant" is that value of [S] allowing the population to grow at rate u(max)/2. An equation describing the behavior of [S] over time, and thus by implication the dynamics of a biodegradable synthetic compound, follows via a simple derivation (36), resulting in Equation 3, in which Y is the "yield coefficient" in cells or biomass produced per unit S metabolized.

$$\frac{dS}{dt} = -\frac{u(max)}{Y} \frac{[S]}{Ks + [S]} N \qquad (3)$$

This equation is difficult to apply in a broader ecological context, however. The first difficulty is mechanical: Equation 3 is non-linear in its parameters, and thus imposes a high cost in computation time when used in a computer code. For trace

concentrations (i.e., [S] << Ks), however, the term (Ks + [S]) in Equation 3 can be approximated by Ks, giving:

$$\frac{d[S]}{dt} = - \frac{u(max)}{Y\ Ks} N\ [S] \qquad (4)$$

This formulation is similar to the "second-order" equations used to describe the kinetics of chemical reactions, and u(max)/(Y Ks) can by analogy be termed a second-order biolysis rate constant Kb2, with units /time/(cells/liter) when population sizes N are expressed in cells/liter.

There are conceptual difficulties as well, however. A natural microbial community derives its energy from a variety of sources. A species restricted to a trace-level synthetic compound as its sole carbon source would be at a severe competitive disadvantage; there is no way to predict the population densities the degrader could attain in real systems. Further, the presence of multiple energy-yielding substrates violates a fundamental assumption of the Monod approach, that is, that [S], the synthetic compound, limits growth. Compounds may be transformed in energy-requiring detoxification processes, making the concept of cell yield (Y) of dubious utility. When the compound is degraded without a change in population size, the zero yield invalidates Equations 3 and 4 alike. This phenomenon is sometimes called "cometabolism" (37).

Still, the rate of transformation of organic pollutants must depend on the structure of the compound and the metabolic capacity of microbial communities. The simplest expression of this duality is the second-order equation:

$$d[S]/dt = - Kb2\ B\ [S] \qquad (5)$$

which asserts that the rate of biolysis (d[S]/dt) is first-order in compound concentration [S] and in microbial activity B, and in which a dogmatic identification of Kb2 with u(max)/(Y Ks) is discarded. This technique is used by most currently operational exposure models.

Logical and Data Structures of Aquatic Fate Codes

Logical Structures. When a synthetic organic chemical is released into an aquatic system, the entire array of transport, transfer, and transformation processes begins at once to act on the chemical. Transport from the point of entry into the bulk of the system takes place by advection and by turbulent dispersion. Transfers to sorbed forms and irreversible transformation processes proceed simultaneously with the transport of the chemical. After the elapse of sufficient time, the chemical comes to be distributed throughout the system, with relatively smooth concentration gradients resulting from dilution, speciation, and

transformation. The most efficient way to describe the parallel action of the processes is to combine them into a mathematical description of their total effect on the rate of change of chemical concentration in the system, via a set of coupled differential equations.

The simplest, and perhaps most important, principle used in constructing environmental models is the conservation law: matter can be neither created nor destroyed. This means that every molecule of a chemical that enters a defined spatial zone (e.g., a laboratory tank or beaker, the epilimnion of a lake, the Earth's atmosphere, etc.) must ultimately either leave the system, be transformed into another compound, or take up residence in the system. The behavior of a chemical in an aquatic system thus can be rigorously described by using the conservation law as an accounting principle. Imagine, first, an accounting boundary drawn around some segment of the environment. This imaginary boundary encloses a "control volume," or accounting unit to be used in a model. In real cases, accounting boundaries are often chosen to correspond with actual physical discontinuities, such as river banks, the air/water interface, the benthic-sediment/water-column interface, the depth of bioturbation of sediments, etc. In many cases, however, the accuracy and detail of a model can be improved by including many relatively small accounting units bounded only by arbitrary lines drawn on a map or vertical profile of the water body.

Every molecule entering the control volume has three courses available to it: export (movement out of the control volume), transformation, or residence. Environmental modeling thus begins by writing a mass balance around the control volume. This mass balance expresses the changes in concentration (that is, increases and decreases in the number of chemical molecules resident per unit volume of the segment) that result from loadings (i.e., inputs), exports, and transformations. The product of concentration [C] (mass/volume) and volume V is the accountable mass, so, using the usual notation of differential equations to denote a rate of change (that is, d[C]/dt denotes the rate of change of concentration [C] per unit time t):

$$V\, d[C]/dt = Lo - Ex - V\, k\, E\, [C] \qquad (6)$$

that is, mass change rate = load - export - transformations,

where E is the environmental factor driving the transformation of the compound (e.g., $[H^+]$), and k is the kinetic constant of the reaction pathway. If we consider water-borne exports only, Ex can be set equal to (F)[C], where (F) is the flow rate of water leaving the system in volume/time. The second-order transformation process k E [C] must have units mass/volume/time; multiplication by V converts it to the proper units (mass/time).

Dividing both sides of Equation 6 by V gives a unit equation for modeling chemical concentrations in real systems:

$$d[C]/dt = Lo/V - (F/V)[C] - k\ E\ [C] \qquad (7)$$

(The term (V/F) has units of time; when V and F apply to an entire system, (V/F) is often called the "hydraulic residence time" or "detention time" of the water body.)

Models of real ecosystems often consist of many unit control volumes coupled together by transport equations. An export from one unit then becomes a load on another. The loadings (Lo) on each control volume can thus be the sum of many terms, including "external" chemical loadings from industrial or agricultural discharges, contaminated rainfall, etc., plus the "internal" loadings due to hydrodynamic motions and other transport cycles within the system that move chemicals from one control volume to another. In models that include both parent compounds and transformation products, the rate of transformation of the parent to the product (k E [C]) is also an internal loading (Lo/V) of the product chemical.

Export processes are often more complicated than the expression given in Equation 7, for many chemicals can escape across the air/water interface (volatilize) or, in rapidly depositing environments, be buried for indeterminate periods in deep sediment beds. Still, the majority of environmental models are simply variations on the mass-balance theme expressed by Equation 7. Some codes solve Equation 7 directly for relatively large control volumes, that is, they operate on "compartment" or "box" models of the environment. Models of aquatic systems can also be phrased in terms of continuous space, as opposed to the "compartment" approach of discrete spatial zones. In this case, the partial differential equations (which arise, for example, by taking the limit of Equation 7 as the control volume goes to zero) can be solved by finite difference or finite element numerical integration techniques.

Data Structures. Inspection of the unit simulation equation (Equation 7) indicates the kinds of input data required by aquatic fate codes. These data can be classified as chemical, environmental, and loading data sets. The chemical data sets, which are composed of the chemical reactivity and speciation data, can be developed from laboratory investigations. The environmental data, representing the driving forces that constrain the expression of chemical properties in real systems, can be obtained from site-specific limnological field investigations or as summary data sets developed from literature surveys. Allochthonous chemical loadings can be developed as worst-case estimates, via the outputs of terrestrial models, or, when appropriate, via direct field measurement.

From these data, aquatic fate models construct outputs delineating exposure, fate, and persistence of the compound. In general, exposure can be determined as a time-course of chemical concentrations, as ultimate (steady-state) concentration distributions, or as statistical summaries of computed time-series. Fate of chemicals may mean either the distribution of the chemical among subsystems (e.g., fraction captured by benthic sediments), or a fractionation among transformation processes. The latter data can be used in sensitivity analyses to determine relative needs for accuracy and precision in chemical measurements. Persistence of the compound can be estimated from the time constants of the response of the system to chemical loadings.

Available Aquatic Fate Codes

Although many research models and water quality codes have been written in recent years, relatively few finished codes for synthetic organics in aquatic systems are available to non-specialists. Useful codes must include some form of the second-order process models described above, be written as general purpose codes (i.e., not as regression models), have some form of written documentation and user manual, and be publicly available in a portable high-level language. All the codes listed below survive these tests. All are written in FORTRAN IV; FORTRAN compilers are virtually universally available. A brief description of the main available codes follows. The references given in these paragraphs include documentation and sources for additional information and copies of the computer programs. These codes are, for the most part, undergoing continuing revision and test by their authors, so detailed comparisons are problematic and are not attempted. The documentation reports cited for the codes may not fully describe the currently available programs; direct contact with code authors is advisable.

A code developed for the Chemical Manufacturers Association by HydroQual (SLSA, or Simplified Lake and Stream Analyzer 38, 39) deserves careful study for its insightful exploration of the general characteristics of the behavior of hydrophobic materials in aquatic systems. This code, with its documentation report, provides an excellent entry point to the field.

EXAMS1/EXAMS2. The EXposure Analysis Modeling System (EXAMS, 40) was developed as a screening tool for estimating long-term fate, residual concentrations, and persistence. Although written in full differential equation form, the program invokes a special routine for deriving steady-state solutions, so as to simplify evaluation of long-term chemical loadings. EXAMS can accept one, two, or three-dimensional compartment models of aquatic systems. A follow-on version (EXAMS2) computes the fate of transformation products and allows direct user access to initial conditions and simulation intervals.

HSPF. The Hydrologic Simulation Program (FORTRAN) (41, 42) is based on the Stanford Watershed Model. Version 7 of HSPF incorporates the process models of SERATRA in its aquatic section, with several (user-selectable) options for sediment transport computations. HSPF includes the generation of transformation products, each of which is in turn subject to volatilization, phototransformation, biolysis, etc.

PEST. This code (43) was developed within the framework of Rensselaer Polytechnic Institute's CLEAN (Comprehensive Lake Ecosystem Analyzer) model. It includes highly elaborated algorithms for biological phenomena, as described in this volume (44). For example, biotransformation is represented via second-order equations in bacterial population density (Equation 5) in the other codes described in this section; PEST adds to this effects of pH and dissolved oxygen on bacterial activity, plus equations for metabolism in higher organisms. PEST allows for up to 16 compartments (plants, animals, etc.), but does not include any spatially resolved computations or transport processes other than volatilization.

SRI/SERATRA/TODAM/FETRA/CMRA. Based on a summary of process models published by Stanford Research Institute (SRI model, 45), Battelle Pacific Northwest Laboratories' SERATRA (Sediment-Radionuclide Transport Model) was expanded from its original first-order radionuclide decay to include process models for photolysis, hydrolysis, oxidation, biolysis, and volatilization (46). The SERATRA code is an unsteady, two dimensional (longitudinal and vertical) finite element code for transport of dissolved constituents and transport, deposition, and resuspension of sediments and sorbed contaminants. A one-dimensional (longitudinal) version (TODAM) and a two-dimensional (longitudinal and lateral) estuarine version (FETRA) are also available from BPNL. These codes require hydrodynamic conditions over time as input to the programs. Sorption/desorption are treated as kinetic processes first-order in chemical concentrations. A set of codes directly useful in environmental safety evaluations (CMRA, Chemical Migration and Risk Assessment) was also developed for use with the SERATRA program (47). CMRA also includes a non-point-source loading model for agricultural sources, a hydrodynamic code, and a toxicological post-processor FRANCO (FRequency ANalysis of pesticide COncentrations for risk assessment) that assembles time-series data on chemical concentrations into an analysis of the frequency and duration of toxic stress events.

TOXIC. This code (48-51) was developed at the University of Iowa as an elaboration of the SRI model. To its predecessor, it adds a fish uptake and depuration model and expanded dynamic capabilities. The code was developed during the course of field

studies of the behavior of pesticides and herbicides in Iowa reservoirs.

UTM-TOX. The Unified Transport Model for Toxicants (UTM-TOX, 52) was developed at Oak Ridge National Laboratory (ORNL) on the base of the ORNL Unified Transport Model (UTM), itself under development from the early 1970's. UTM-TOX includes air, water, and terrestrial submodels. The aquatic fate submodel includes volatilization, hydrolysis, biolysis, photolysis, and sorption equilibria. Sorbed phases are assumed unreactive in the 1982 version.

WASP/TOXIWASP/WASTOX. The Water Quality Analysis Simulation Program (WASP, 53)is a generalized finite-difference code designed to accept user-specified kinetic models as subroutines. It can be applied to one, two, and three-dimensional descriptions of water bodies, and process models can be structured to include linear and non-linear kinetics. Two versions of WASP designed specifically for synthetic organic chemicals exist at this time. TOXIWASP (54) was developed at the Athens Environmental Research Laboratory of U.S. E.P.A.; WASTOX (55) was developed at HydroQual, with participation from the group responsible for WASP. Both codes include process models for hydrolysis, biolysis, oxidations, volatilization, and photolysis. Both treat sorption/desorption as local equilibria. These codes allow the user to specify either constant or time-variable transport and reaction processes.

All these codes vary slightly in implementation, resulting in slightly different input data. For example, some use standard Arrhenius functions to express temperature dependencies; others use the civil engineering power equation. Although equivalent, the input data differ. Again, some codes use the 39 wavelength intervals specified by the SOLAR photochemical code (24); others use an 18 increment version from SERATRA. A few codes do not include a term for atmospheric resistance to volatilization, and thus require caution when used for compounds with Henry's Law constants smaller than 0.001 atm-m^3/mole (23). At present, only HSPF and EXAMS2 include transformation product capabilities, and only the EXAMS codes include a full treatment of ionizable compounds and ion-specific chemical reactivities. It should be said, however, that most of the currently active code authors are aware of the limitations of their codes and are actively engaged in further development.

Although all these codes have been tested for theoretical integrity and realism to some extent, few appropriate data sets for model testing are available and standardized methods for collecting them are only now under development (56). At this time, a full evaluation of a chemical is perhaps best accomplished using several fate codes, with careful comparisons among the outputs of the codes.

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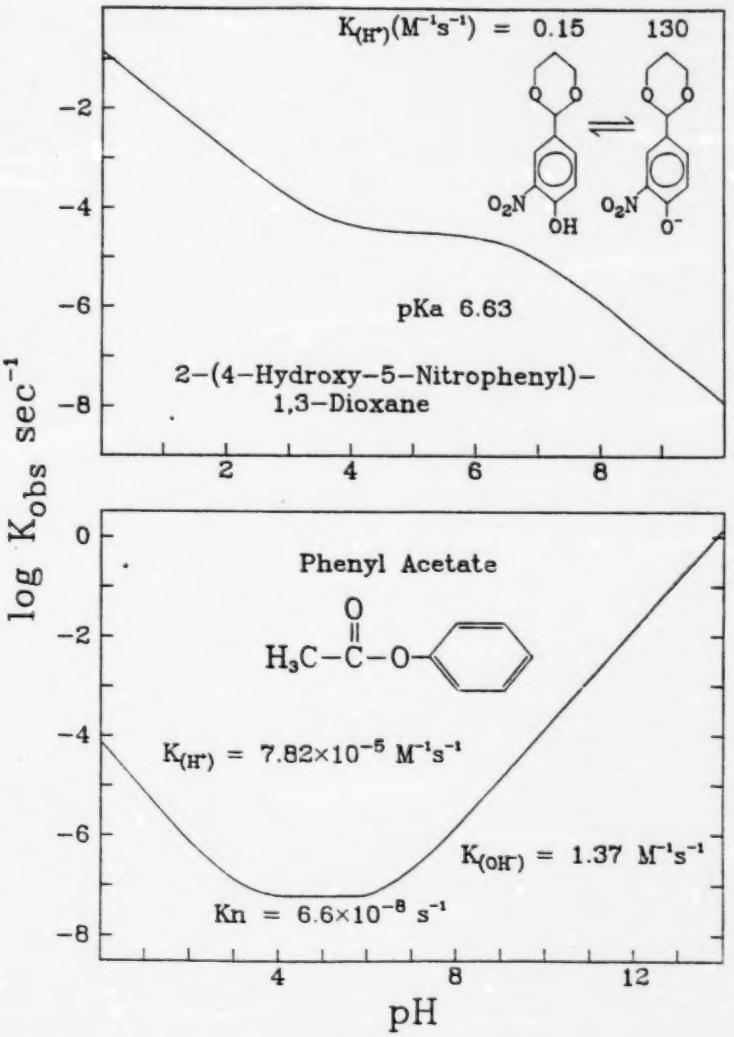

1. Hydrolysis pH-rate profiles of phenyl acetate (lower) and a substituted 2-phenyl-1,3-dioxane (HND). Phenyl acetate profile constructed from data of Mabey and Mill (32), HND profile from data of Bender and Silver (33). Phenyl acetate reacts via specific-acid catalyzed, neutral, and base-catalyzed transformation pathways. The pseudo-first-order rate constant is given by $K_{obs} = K_{(H^+)}[H^+] + K_n + K_{(OH^-)}[OH^-]$. HND hydrolyzes only via an acid-catalyzed pathway; the phenolate anion is some 867 times more reactive than its conjugate acid. In this case, $K_{obs} = (0.15\ I_o + 130(1-I_o))[H^+]$ (see Equation 1).